III.A.16 Surface-Modified Ferritic Interconnect Materials for Solid Oxide Fuel Cells

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Objectives

- Engineer a surface oxide scale on a ferritic stainless steel that is
  - Mechanically and chemically stable at 800°C in oxidizing and reducing environments, and
  - Electrically conductive to minimize stack internal resistance losses.
- Develop process for rendering the alumina scale electrically conductive (such as metal ion implantation) that is inherently scaleable for manufacturing.
- Demonstrate stable electrical conductivity of interconnects for an extended time (>1000 hours) at 800°C in contact with cathode materials ($(La_{0.8}Sr_{0.2})FeO_3$ [LSF] and $(La_{0.6}Sr_{0.4})(Fe_{0.8}Co_{0.2})O_3$).

Approach

- Formation and characterization of stable alumina/chromia scales on ferritic stainless steels, such as FeCrAlY and 430.
- Doping of near-surface layer with elements such as niobium, titanium, and yttrium to render the insulating alumina scale conductive.
- Exposure testing, via DC area specific resistance (ASR) and AC impedance measurements, of treated ferritic stainless steel samples at elevated temperatures (800°C) in air for up to 1000 hours, including elevated temperature testing/characterization of interconnect/LSF cathode diffusion.

Accomplishments

- Formed and demonstrated stable (up to 900°C), self-limiting scale on FeCrAlY in oxidizing environments and in contact with LSF cathode materials.
- Observed an order-of-magnitude decrease in ASR with the implantation of niobium or titanium at a dose of $1x10^{16}$ atoms/cm^2, as compared to un-doped FeCrAlY (resistance comparable to chromia-forming 430 SS).
- Established conduction mechanism of doped and un-doped FeCrAlY scales using AC impedance techniques and confirmed that results agreed with ASR measurements.
- Demonstrated stability of doped and un-doped FeCrAlY scales in contact with LSF cathode material at elevated temperatures (800°C) in exposure tests for 1000 hours.

Future Directions

- Conduct additional tests to establish optimum dopant concentrations (and type) in order to ensure low ASR and minimum effect due to bulk diffusion.
- Having established proof-of-concept of the proposed ion implantation methodology, the next step will be to develop more scaleable manufacturing processes that achieve the same oxide composition, e.g. magnetron sputtering , sol-gel or other similar processes.

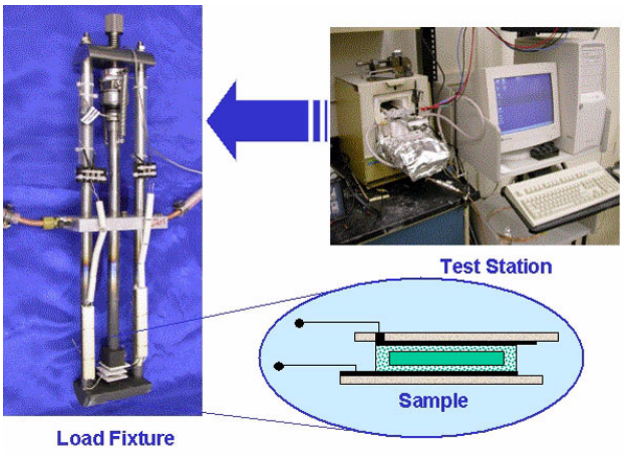

Figure 1. Load Fixture and Corresponding Test Station for High-Temperature DC ASR and AC Impedance Measurements

Introduction

Interconnects are a critical element of a solid oxide fuel cell (SOFC) assembly in that they must: 1) be easily formable and machinable; 2) be thermally matched to adjoining ceramic cell components; 3) have mechanical integrity and fracture toughness over prolonged periods of exposure to high temperature, reducing/oxidizing environments; and 4) develop surface scales that are not only stable and electrically conductive over a large O_2 concentration range, but prevent ion migration or gas permeation across the interconnect-electrode boundary. Although much work has focused on metal alloys for interconnect materials, particularly chromium alloys containing an oxide that is both oxidation resistant and electrically conductive, the thermal instability of typical native metal oxides allows interdiffusion of cations across the interconnect-electrode boundary that ultimately leads to degradation of SOFC performance. In particular, the volatility and corresponding outward diffusion tendencies of chromium cations in chromia scale-forming alloys lead to spallation and instability at the interconnect/electrode boundary.

Approach

A novel approach, based on ion implantation, was investigated to render the stable alumina scale on aluminum-containing ferritic alloys, such as FeCrAlY, conductive. As part of the one-year effort, we implanted a series of pre-treated FeCrAlY stainless steel samples with niobium and titanium ions and, alongside sibling 430 stainless steel samples (as control), conducted both DC ASR and AC impedance measurements to evaluate ASR and conduction mechanisms. In addition to evaluating FeCrAlY and 430 scale formation and properties up to 900°C in air for 1,000 hours, the stability of the scales were evaluated in contact with LSF cathode materials. A specially designed load frame (fixture), shown in Figure 1, was designed and fabricated in order to accurately control the applied load at the contacting interfaces at the elevated temperatures for this investigation. Scale structure and composition were evaluated with x-ray diffraction (XRD) and energy dispersive x-ray (EDX)/Auger electron spectroscopy (AES), respectively.

Results

Oxidation kinetics for both FeCrAlY and a typical chromia-forming ferritic steel (430) were investigated. We confirmed, as part of our oxidation kinetics evaluation of FeCrAlY and 430 ferritic steel, the parabolic growth of a mixed chromia/alumina scale on FeCrAlY and a single chromia layer in the case of the 430 stainless steel; the outer contiguous layer of Al_2O_3, in the case of FeCrAlY, formed a stable, self-limiting, protective scale. To render the alumina scale conductive, we then implanted either titanium or niobium ions into FeCrAlY scales to a fixed depth, varying only the thickness of the oxide. Area specific resistance (ASR) was measured as a function of temperature and time at temperature using both modified 4-point DC and AC impedance techniques. As a result of the relatively high lead/system resistance component of the overall ASR measurement, a consequence of the test configuration, a qualitative measurement of the DC resistance was obtained using an oxidized 430 SS specimen as a means for comparison. ASR for an un-doped FeCrAlY oxide scale (i.e., alumina) was more than an order of magnitude greater than the 430 control sample, whereas the ASR for the doped FeCrAlY oxide scale sample was comparable to the 430 control sample; hence, the resistance of a doped alumina scale on FeCrAlY was equal to the resistance of a chromia-scale forming alloy, such as 430 (typically <0.1 Ω-cm).

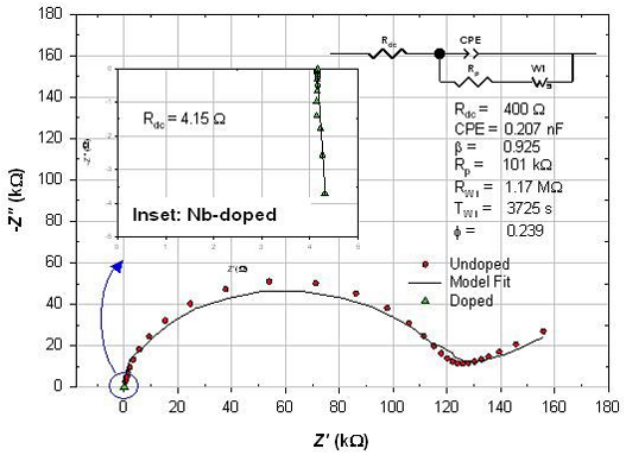

Figure 2. AC Impedance Plot for Un-doped and Nb-doped FeCrAlY Alumina Scales after 1000 Hours at 800°C in Air; Enlarged View around Origin Shown by Inset

Along with the DC ASR measurements, AC impedance measurements were used to assess basic conduction mechanisms across the various interfaces of the contact up to 800°C, providing confirmation of the effect of the dopant. Based on the AC impedance results, un-doped alumina scales exhibited mixed conduction and the transport-limited mechanisms of a high-impedance, solid-state electrolyte. Addition of niobium resulted in at least a two-order-of-magnitude reduction in resistance over the un-doped specimen. Niobium-doped alumina scales exhibited pure electronic conduction, as opposed to mixed ionic-electronic conduction, even after 1000 hours at 800°C. As shown in Figure 2, the DC resistance component was less than the system resistance (i.e., leads, junctions, etc.).

A diffusion couple experiment, placing a doped FeCrAlY alumina scale in contact with an LSF cathode material for 1000 hours at 800°C, confirmed the stability of the interface region. The entire diffusion couple specimen, along with fixture, was cross-sectioned and then polished prior to an EDX analysis to produce the elemental "dot" maps shown in Figure 3. No detectable cation interdiffusion took place across the contiguous alumina layer, and thickness of the scale layer remained essentially unchanged after 500 hours at temperature. This stability of the alumina scale on FeCrAlY is consistent with its reported long-term stability

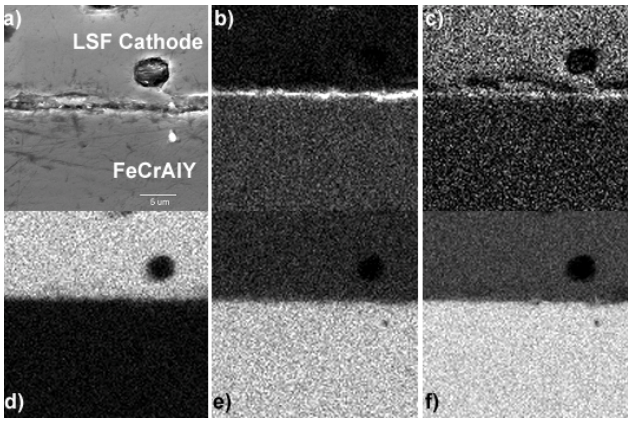

Figure 3. LSF/FeCrAlY Contact @ 800°C for 1000 Hours (intimate contact); SEM and X-ray Dot Maps for: a) SEM, b) Aluminum, c) Oxygen, d) Lanthanum, e) Chromium, and f) Iron

(~40,000 hours at 950°C) in advanced gas-cooled reactors for the nuclear industry.

Conclusions

Our results have clearly shown that dopant additions increase the electronic conductivity of alumina-forming scale alloys, such as FeCrAlY, transforming from a mixed ionic/electronic conduction mechanism. Just as importantly, the demonstrated stable formation of an alumina scale is a clear advantage over conventional pure chromia forming alloys for interconnect materials. Future work in this area would be to optimize the dopant addition/concentration and any possible effects of bulk dilution (although none were observed in the limited 1000 hour tests of this study), as well as the type of dopant addition; i.e., strontium and TiO_2 as opposed to pure titanium. Since we have proved the concept of this procedure (patent application submitted) the next step would be to develop more scaleable manufacturing processes that achieve the same oxide composition, e.g. by magnetron sputtering, sol-gel, or other similar processes.

References

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FY 2004 Publications/Presentations

1. 2003 Fuel Cell Seminar, Miami, FL.
2. 13th International Conference on Surface Modification of Materials by Ion Beams, September, 2003, San Antonio, TX.

Special Recognitions & Awards/Patents Issued

1. One patent pending